

PATENT ABSTRACTS OF JAPAN

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(54) MANUFACTURE OF COLUMN PACKING FOR CHROMATOGRAPHY

(57)Abstract:

PURPOSE: To suppress the secondary action caused by residual silanol group and prevent the tailing of peak by reacting a specified compound with a carrier represented by silica gel.

CONSTITUTION: This packing is manufactured by reacting a compound represented by the formula with a carrier represented by silica gel. In the formula, R1, R2, R3, R4, R5, and R6, which may be the same or different, each represent an alkyl group having 1-30 carbon atoms, R represents an alkyl group having 1-30 carbon atoms or X (cyano group, phenyl group, trifluoro group, vinyl group, mercapto group, or aldehyde group), and (n) represents 1-2000. Physical properties such as particle form, pore diameter, and surface area of the silica gel to be used are not particularly limited, and a proper one can be selected according to the purpose of use. Thus, a troublesome end cap operation can be omitted to provide the packing. This packing can prevent the tailing of peak of basic compounds or phenols.



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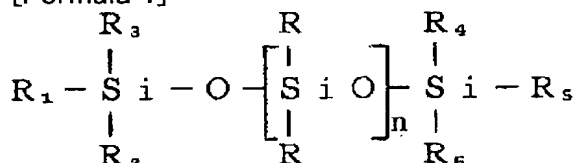
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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the bulking agent for chromatographies which the compound expressed with the following formula I (** 1) to **** represented by silica gel is made to react, and does not produce tailing of the peak by the residual silanol group.

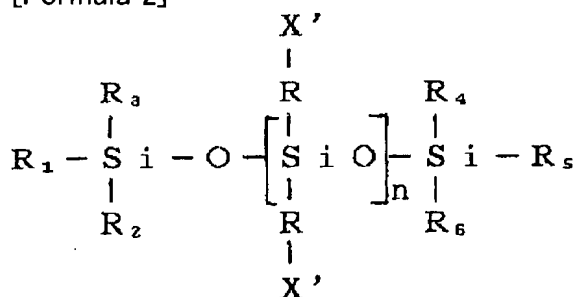
[Formula 1]



by the alkyl group of carbon numbers 1-30, it may be the same the inside R1, R2, R3, R4, R5, and R6 of a formula, or it may differ. R is the alkyl group or X (the cyano group, the phenyl group, the trifluoro radical, the vinyl group, the sulfhydryl group, aldehyde group) of carbon numbers 1-30. n is 1-2000.

[Claim 2] The manufacture approach of the bulking agent for chromatographies which the compound expressed with the following formula II (** 2) to **** represented by silica gel is made to react, and does not produce tailing of the peak by the residual silanol group.

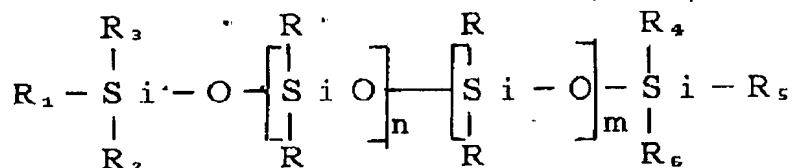
[Formula 2]



by the alkyl group of carbon numbers 1-30, it may be the same the inside R1, R2, R3, R4, R5, and R6 of a formula, or it may differ. R is the alkyl group or X (the cyano group, the phenyl group, the trifluoro radical, the vinyl group, the sulfhydryl group, aldehyde group) of carbon numbers 1-30. n is 1-2000. X' is a cyano group, a phenyl group, a trifluoro radical, a vinyl group, a sulfhydryl group, an aldehyde group, and -H.

[Claim 3] The manufacture approach of the bulking agent for chromatographies which the compound expressed with the following formula III (** 3) to **** represented by silica gel is made to react, and does not produce tailing of the peak by the residual silanol group.

[Formula 3]



the inside R1, R2, R3, R4, R5, and R6 of a formula is the alkyl group or X (the cyano group —) of carbon numbers 1–30 A phenyl group, a trifluoro radical, an aldehyde group, a vinyl group, a sulfhydryl group, the combination of the amino group, an imino group or an alkyl group, and X, and R — the alkyl group of carbon numbers 1–30, or X' (a cyano group —) 1–2000m of the combination of a phenyl group, a trifluoro radical, an aldehyde group, a vinyl group, a sulfhydryl group, an aldehyde group, a hydroxyl group, the amino group, an imino group, –H, or alkyl group and X' and n are 1–2000.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

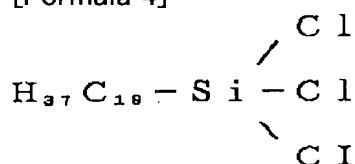
[0001]

[Industrial Application] This invention relates to the manufacture approach of a liquid and the bulking agent for gas chromatographies.

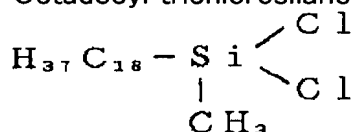
[0002]

[Description of the Prior Art] Conventionally, what combined compounds, such as an alkyl group, with the active group which exists in a carrier surface like the silanol group on the front face of silica gel as a bulking agent for liquid chromatography is used. The octadecyl silica gel bulking agent (ODS) especially using an octadecyl silane is used widely. There is the following as a common reagent used in order to manufacture this ODS.

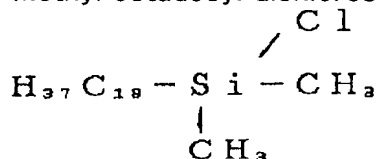
[Formula 4]



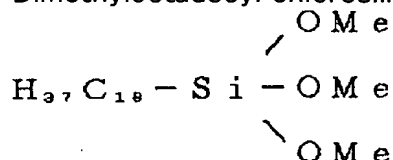
Octadecyl trichlorosilane [** 5]



Methyl octadecyl dichlorosilane [** 6]



Dimethyloctadecyl chlorosilane [** 7]



Octadecyltrimethoxysilane [0003] Si-Cl serves as a reaction radical and chlorosilane carries out a chemical bond. Si-OMe and Si-OEt serve as a reaction radical, and alkoxy silane like a methoxy silane joins together. In addition, silazanes N-Si-N and cyclosiloxane are also used for a reaction with a silanol group.

[0004] Very, also when an octadecyl silica gel bulking agent was used, it was not avoided that a silanol group remains on a silica gel front face. In this case, a residual silanol group was not able

to press down a secondary operation of the adsorption considered as a cause, and an ion-exchange-operation.

[0005]

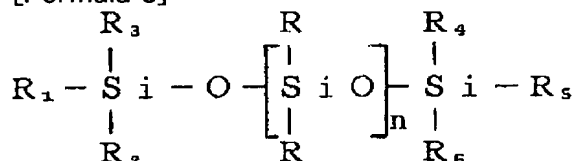
[Problem(s) to be Solved by the Invention] For this reason, the problem was in the repeatability of chromatogram according to the tailing phenomenon of a peak, the delay of the elution of special material, etc. Then, after combining an alkyl group with the silanol of silica gel in order to press down a secondary operation of a residual silanol group, carrying out end cap actuation, using the so-called end cap agent as an activity which inactivates a silanol group further is performed. However, when using it for phenols also by end cap actuation, it cannot be said that it is perfect.

[0006]

[Means for Solving the Problem] This invention takes the above-mentioned point into consideration, although an oxine copper peak is broadcloth without carrying out ***** end cap actuation of trouble, it appears, it presses down the secondary operation to which a residual silanol group is considered as a cause, and uses as a proposal plug the manufacture approach of a bulking agent that a basic compound or phenols does not produce tailing of a peak, either.

[0007] In order to attain this purpose, this invention is characterized by making the compound expressed with the following formula I (** 8) to **** (henceforth silica gel) represented by silica gel react.

[Formula 8]

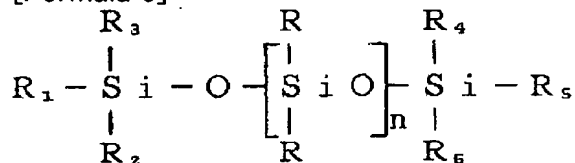


by the alkyl group of carbon numbers 1-30, it may be the same the inside R1, R2, R3, R4, R5, and R6 of a formula, or it may differ. R is the alkyl group or X (the cyano group, the phenyl group, the trifluoro radical, the vinyl group, the sulfhydryl group, aldehyde group) of carbon numbers 1-30. n is 1-2000.

[0008]

[Example] Hereafter, it explains in detail per this invention. This invention makes a following-type I (** 9) compound react to silica gel.

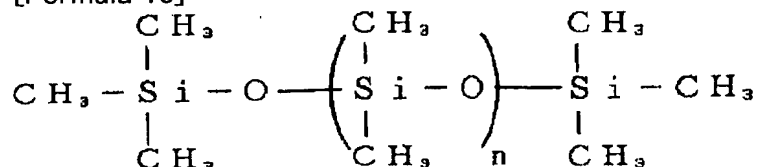
[Formula 9]



by ****, by the alkyl group of carbon numbers 1-30, R1, R2, R3, R4, R5, and R6 may be the same, or they may differ. R is the alkyl group or X (the cyano group, the phenyl group, the trifluoro radical, the vinyl group, the sulfhydryl group, aldehyde group) of carbon numbers 1-30. n is 1-2000. Moreover, there is no limit in physical-properties values, such as particle shape of the silica gel used for this invention and pore size, and surface area, and it can be suitably chosen as them according to the purpose of use.

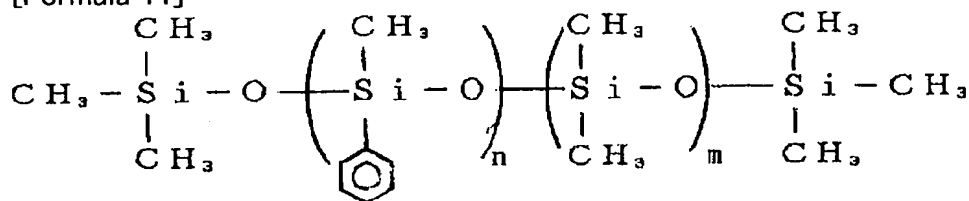
[0009] When the compound used for this invention is described, there is poly dimethylsiloxane (** 10) as an example.

[Formula 10]



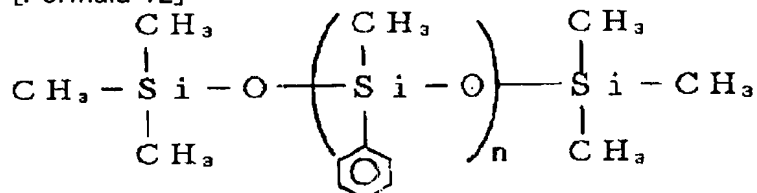
In the example of a trade name, silicone OV-1, silicone OV-101, DC200, etc. are near. Moreover, there is polyphenyl methyl dimethylsiloxane (** 11).

[Formula 11]



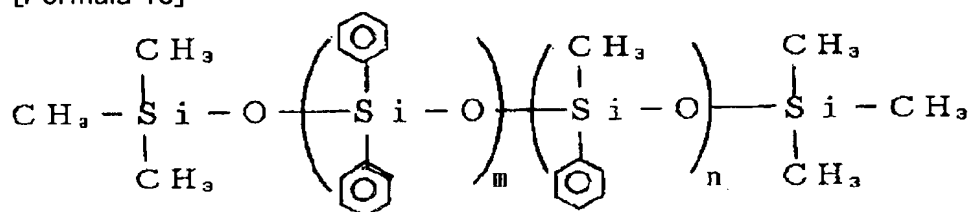
In the example of a trade name, silicone OV-3, silicone OV-7, silicone OV-11, etc. are near. Furthermore, there is a polyphenyl methyl siloxane (** 12).

[Formula 12]



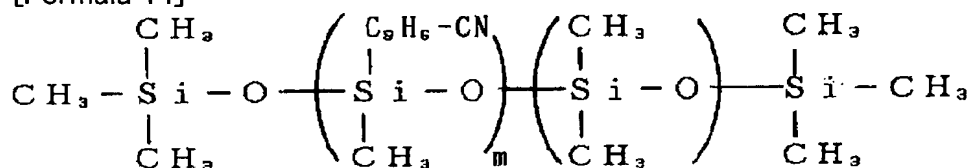
In the example of a trade name, silicone OV-3 etc. are near. In addition, there are poly diphenyl dimethylsiloxane (** 13), poly cyano propylmethyl dimethylsiloxane (** 14), and a PORISHIANO propylmethyl phenylmethyl siloxane (** 15).

[Formula 13]



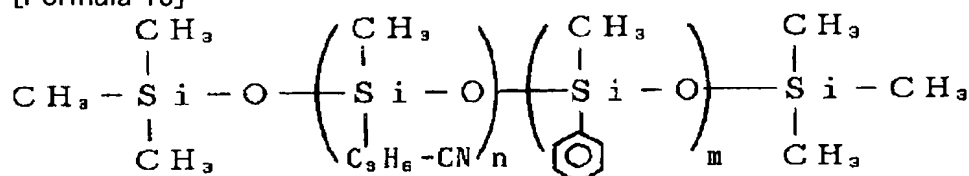
In the example of a trade name, silicone OV-61 etc. are near.

[Formula 14]



In the example of a trade name, silicone OV-105 etc. are near.

[Formula 15]



In the example of a trade name, silicone OV-225 etc. are near.

[0010] A well-known gaseous-phase method and a liquid membrane method can be conventionally used for making the compound of Formula I react to silica gel in this invention. **** other than silica gel can use a diatomaceous earth system, a refractory brick system, a titania, a zirconia, etc. here.

[0011] [Example 1] Reaction of a methyl cyano propyl polysiloxane and silica gel.

Hexadecane 30ml, often dried silica gel 3g, and a methyl cyano propyl polysiloxane (molecular

weight is about 10,000) are often mixed to 100ml round bottom flask, and it flows back by tying to a cooling pipe. It cools radiationally to a room temperature after 7-hour reflux. Washing filtration of silica gel is performed after this. This sequence performs the solvent to be used by dichloromethane 100ml, methanol 100ml, and acetone 50ml. Thus, the obtained cyano propyl qualification silica gel performs slurry restoration in stainless steel tubing, after often drying, and it uses it for analysis as a packed column for HPLC.

(Example of analysis) Chromatogram ([drawing 1](#))

analysis condition: — eluate: — acetonitrile / water =20/80 column temperature: — 40-degree-C rate-of-flow: — 1.0 ml/min detector: — UV254nm sample: — acetophenone **, benzene **, toluene **, and naphthalene **.

[0012] [Example 2] Reaction of dimethylpolysiloxane and silica gel.

Silica gel is dried under 180-degree-C reduced pressure for 15 hours for a reaction. The silica gel is put into the ampul for a reaction with a reagent. And a sink and enclosure are performed for desiccation N2. The ampul is placed into the oven for heating, and it raises with the programming rate of 4 degrees C / min to 300 degrees C. After the reaction of 15 hours, ampul is cooled, it opens and washing filtration of the embellished silica gel is performed. This sequence performs the solvent to be used by dichloromethane 100ml, methanol 100ml, and acetone 50ml. Thus, the obtained methyl group qualification silica gel performs slurry restoration in stainless steel tubing, after often drying, and it uses it for analysis as a packed column for HPLC.

Bibliography: Journal of High Resolution Chromatography & ChromatographyCommunication.Vol.18 (1985) 709.

(Example of analysis) Chromatogram ([drawing 2](#))

analysis condition: — eluate: — acetonitrile / water =40/60 column temperature: — 40-degree-C rate-of-flow: — 1.0 ml/min detector: — UV254 sample: — acetophenone **, benzene **, toluene **, and naphthalene **.

[0013] [Example 3] Reaction of a methyl octadecyl polysiloxane and silica gel.

The approach is the same as that of said example 2.

(Example of analysis) Chromatogram ([drawing 3](#))

analysis condition: — eluate: — acetonitrile / water =50/50 column temperature: — 40-degree-C rate-of-flow: — 1.0 ml/min detector: — UV254 sample: — acetophenone **, benzene **, toluene **, and naphthalene **.

(Example of analysis) Chromatogram ([drawing 4](#))

analysis condition: — eluate: — acetonitrile / water =30/70 column temperature: — 40-degree-C rate-of-flow: — 1.0 ml/min detector: — UV254 sample: — pyridine ** and phenol **.

(Example of analysis) Chromatogram ([drawing 5](#))

analysis condition: — eluate: — acetonitrile / 20mM phosphoric-acid =5/95 column temperature: — 40-degree-C rate-of-flow: — 1.0 ml/min detector: — UV240nm sample: — oxine copper.

[0014] [Example 4] The methyl octadecyl polysiloxane was made to react to the silica gel for gas chromatography of 80-100 meshes similarly, and the bulking agent for gas chromatography was obtained. Tapping restoration was carried out and the obtained bulking agent was used for analysis at the 3phix2m glass column.

(Example of analysis) Chromatogram ([drawing 6](#))

column oven temperature: — 120-degree-C rate-of-flow: — N2 40 ml/min detector: — TCD sample: — n pentane 1, chloroform 2, the n-hexane 3, benzene 4, the n-heptane 5, toluene 6, n-octane 7, ethylbenzene 8, meta xylene 9, O-xylene 10, and n-nonane 11.

[0015]

[Effect of the Invention] According to this invention like the above, the end cap actuation which trouble requires can be omitted, a bulking agent can be obtained, this bulking agent can press down the secondary operation to which a residual silanol group is considered as a cause, and can prevent generating of tailing of peaks, such as a base-like compound and phenols, and ** can also obtain an effective bulking agent very easily.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Chromatogram which carried out high performance chromatography using this invention bulking agent.

[Drawing 2] Chromatogram which carried out high performance chromatography using this invention bulking agent.

[Drawing 3] Chromatogram which carried out high performance chromatography using this invention bulking agent.

[Drawing 4] Chromatogram which carried out high performance chromatography using this invention bulking agent.

[Drawing 5] Chromatogram which carried out high performance chromatography using this invention bulking agent.

[Drawing 6] Chromatogram which carried out the gas chromatography using this invention bulking agent.

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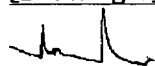
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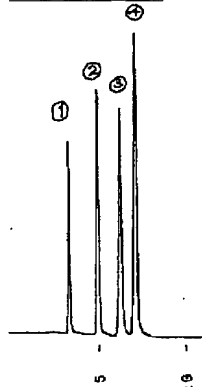
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DRAWINGS

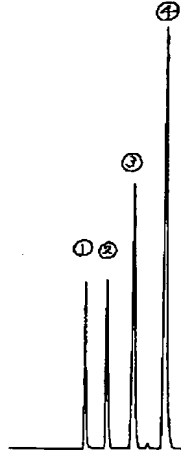
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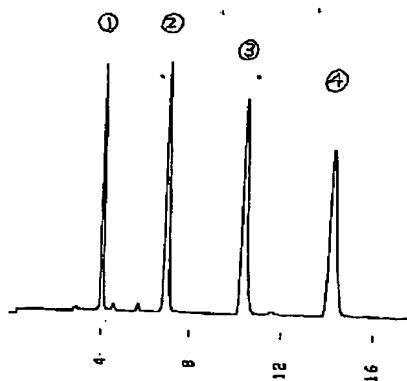
[Drawing 1]



[Drawing 2]



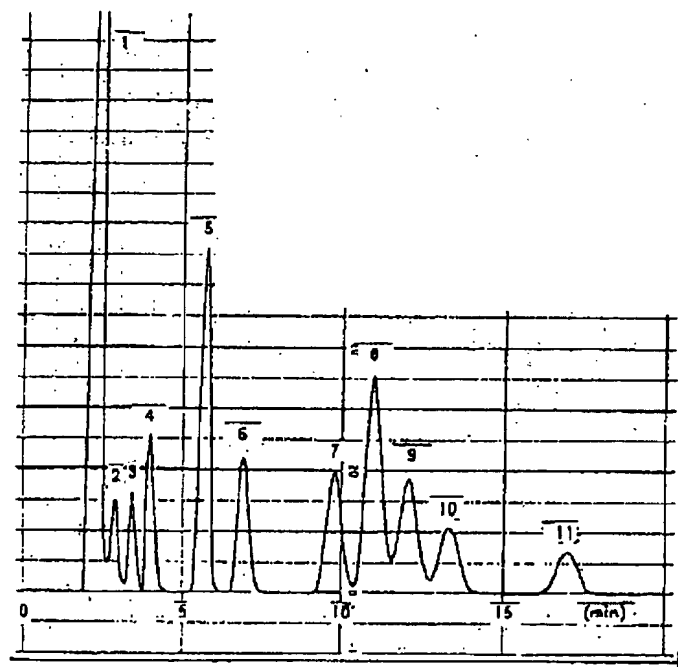
[Drawing 3]



[Drawing 4]



[Drawing 6]



[Translation done.]